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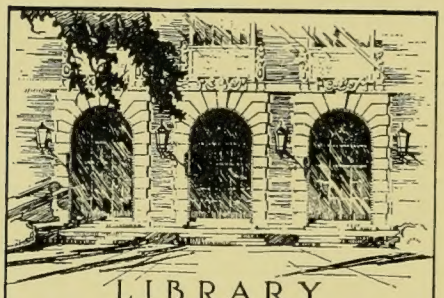

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SIGNIFICANCE OF PESTICIDE RESIDUES: PRACTICAL FACTORS IN PERSISTENCE

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SIGNIFICANCE OF PESTICIDE RESIDUES: PRACTICAL FACTORS IN PERSISTENCE

GEORGE C. DECKER

OBVIOUSLY ALL FACTORS THAT INFLUENCE the magnitude of pesticide deposits or the persistence of residues have some practical value or significance, and one finds it difficult to classify the factors involved as either practical or theoretical. Here the question of practicality is really one of rationality—in other words, correlation of the soundness of the evaluations we have placed on every one of the known factors with the efficiency with which we have utilized the available knowledge.

Until quite recently the insecticides in common use could be divided into groups, such as the highly volatile fumigants, the rather unstable botanicals, and the stable and persistent metallic salts. Thus it developed that for many years most residue problems were associated with highly stable and practically nonvolatile mineral salts. Once such materials were applied to plants or other surfaces, they might be expected to persist unchanged for indefinite periods of time or until removed by mechanical processes.

FACTORS AFFECTING RESIDUE LOSSES

From time to time investigators working on residue problems have isolated and evaluated some of the various factors that affect the magnitude of residues and their persistence. Most of these factors are fully discussed and summarized in recent text or reference books (Brown 1951; Frear 1942; Shepard 1951) and therefore will not be reviewed here. It is possible, however, that one or more important factors involved have been largely overlooked or grossly underestimated. The terms "vapor pressure" and "evaporation" are seldom given much space, and in many cases are not even mentioned in residue discussions. Perhaps this was fitting and proper so long as we were primarily concerned with the residues of lead arsenate and similar, essentially nonvolatile compounds. We may have erred, however, in following the same old lines of approach when we began to attack problems associated with the use of the chlorinated hydrocarbons and other new, synthetic, organic insecticides.

Very soon after DDT came under intensive study in 1944, Fleck (1944:853), reporting on the "Rate of Evaporation of DDT," concluded that "the loss of DDT from insecticidal spray deposits by volatilization will occur too slowly to be of any importance." Two years later Wichmann et al. (1946:218–233) apparently came to about the same conclusion but did not clearly say so. Unfortunately, in both instances the rate of evaporation was determined by exposing known amounts of DDT crystals (63.36 mg and 200 mg) on glass plates which were weighed at intervals. This method, of course, was not conducive to the production of maximum losses by evaporation.

About the same time, Gunther et al. (1946:624–627), reporting on rather extensive residue studies involving progressive analyses of apple foliage and fruit samples, showed that after 86 days "every treatment showed a loss of from 71 to 95 per cent of the original quantity of DDT deposited." There was no suggestion or implication, however, that even a part of the loss might have been due to evaporation. The final conclusion was merely, "A distinction between mechanical weathering and chemical decomposition has not been attempted in this report."

Fleck (1948:706–708) introduced a noteworthy paper with the following appropriate and highly significant statement, "The residual action of an insecticide is determined by its vapor pressure, its sticking power, its solubility, its absorption into the surface to which it is applied, and its resistance to chemical change." From that point on, however, the theme of the paper is chemical change or decomposition; vapor pressure and evaporation are ignored.

It would appear that most workers have taken their cue from these and similar reports, for although several writers (Hadaway & Barlow 1951:854; Hensill & Gardner 1950:102–107; Walker 1950:123–127) have made some reference to vapor pressure, volatility, or evaporation, no one has come forward to emphasize the importance of evaporation as a factor strongly influencing the rate of residue loss where the chlorinated hydrocarbon insecticides and similar materials are involved. Even where a significant and consistent progressive loss of residue has been noted, the tendency has been to attribute the losses almost entirely to erosion, weather, or chemical decomposition.

More recently, in 1950, the writer and his associates (Decker, Weinman, & Bann 1950:919–927), in reporting

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This was an invitation paper, presented in Milwaukee, Wisconsin, in April, 1952, as part of a symposium sponsored by the American Chemical Society. It was accepted for publication in a contemplated number of the Advances in Chemistry series, but after this and several other manuscripts had gone as far as the galley proof stage, the whole project was abandoned and the series was never published. Meanwhile, Gunther & Blinn and others had received the manuscript and had cited it as "In Press." In response to the many inquiries as to the status and disposition of the manuscript, to clear the record it is being published here. Despite the fact that much progress has been made in the intervening years, in fairness to those who read and commented upon the original manuscript, it is published almost unaltered and exactly the same as it would have appeared had publication been consummated in 1953.

This paper is published by authority of the State of Illinois, IRS Ch. 127, Par. 58.21. It is a contribution from the Section of Economic Entomology of the Illinois Natural History Survey.

Dr. George C. Decker, formerly Principal Scientist and Head of the Section of Economic Entomology, Illinois Natural History Survey, is now retired.

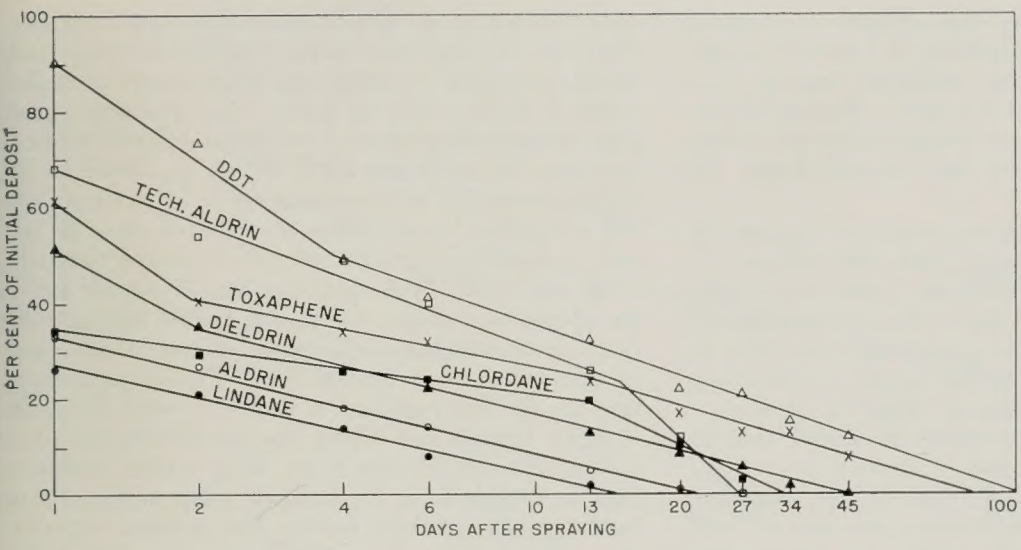

Fig. 1.—Average per cent of initial residue remaining on apple leaves at intervals after spraying with several insecticides.

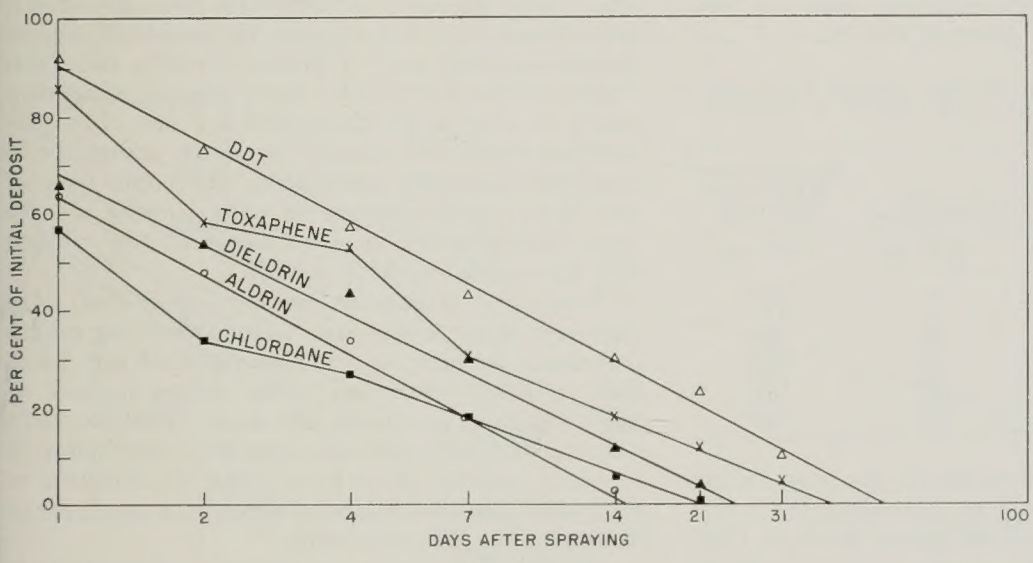

Fig. 2.—Average per cent of initial residue remaining at intervals after red clover was sprayed with several insecticides.

TABLE 1.—Vapor pressure at 25°C. and per cent loss of residue from apple leaves in 10 days for five chlorinated hydrocarbon insecticides.

Insecticide	Vapor Pressure at 25°C.	Per Cent Residue Loss in 10 days
Lindane	0.000,010	95
Aldrin	0.000,052	89
Chlordane	0.000,010	80
Dieldrin	0.000,002,5	65
DDT	0.000,000,3	46

residue studies involving apples, peaches, soybeans, alfalfa, and clover, showed that under varied conditions of exposure the residues of lindane, aldrin, chlordane, dieldrin, toxaphene, and DDT tend to disappear in the order named, and usually in about the same relationship. It was shown also that in some cases, at least, the per cent of the initial deposit remaining at intervals was a straight-line logarithmic function of time (Fig. 1 and 2). Evaporation was not clearly established as an important factor in residue loss, but data were presented to show that there was "a considerable loss of even slowly volatile materials during the actual spraying process." Later the apparent correlation between the reported vapor pressures of the compounds in question and the order in which their residues tended to disappear (Table 1) led to the conclusion that volatility might be an important factor in determining residue persistence.

EVAPORATION STUDIES

In the light of the above observations the writer and his associates set about to explore the ramifications of and, if possible, determine the probable importance of this relatively unevaluated factor.

Throughout the investigations reported, the chemical analysis procedure utilized was that devised by Stepanow (1906:4056–4057) with the modification suggested by Fleck (1947:319–324), Umhoefer (1943:383), and Caldwell & Moyer (1935:38–39). The method involves the conversion of organic chlorine to the chloride ion, which is subsequently determined by the Volhard titration

method. The sensitivity of this method is generally considered to be in the neighborhood of 1.0 ppm, though, in the vast majority of cases, replicates were in close agreement down to 0.5 and 0.3 ppm. The use of this method, however, leaves open to speculation the probability that the trends shown may continue below the 1.0 ppm level.

In the process of developing techniques for the vaporization study—which began with the exposure of known quantities of material in petri dishes or on glass slides and terminated in the use of 10 to 50 mg deposits of crystalline material uniformly dispersed over 20 by 20 inch sheets of semicrepe, white filter paper—it was shown that with a large mass of material heaped or piled on a small area the per cent loss in weight at various intervals was very small, but as the mass of material per unit of surface area was decreased, the rate of loss increased. Finally it was found that the residues deposited on filter paper responded to external conditions much the same as did normal residues on plants (Table 2).

TABLE 2.—Residue loss in 14 days' exposure under greenhouse conditions (temperature 80 ± 5°F., R.H. 75 ± 5 per cent) for seven insecticides.

	Per Cent Loss on Glass Plates		Per Cent Loss on 20 by 20 Inch Filter Paper
Insecticide	100-150 mg	10-25 mg	10-50 mg
Parathion	96	—	98.6
Lindane	82	—	95.4
Aldrin	63	90	90.6
Chlordane	50	88	82.0
Dieldrin	41	52	68.0
Toxaphene	24	31	49.0
DDT	21	26	44.0

Under controlled conditions in the laboratory, where many of the variables could be eliminated, the writer and his associates (Decker, Weinman, & Bann 1950: 919–927) found that the data obtained were exceedingly consistent and in most cases, when plotted, all points were on, or in close proximity to, the lines mathematically fitted to the data. Under such conditions, residue losses for eight and, in some instances, more insecticides were compared at five temperatures. In all experiments the order of loss was the same, with lindane disappearing first and DDT last. As was previously reported (Caldwell and Moyer 1935:38–39) for the field experiments, the residue-loss curves for pure compounds showed that the loss was a straight-line logarithmic function of time (Fig. 3). In general, the data for impure substances, such as technical aldrin, chlordane, and toxaphene, when plotted, departed from the straight line and produced typical wavy lines characteristic of mixtures of compounds differing in their volatility. This was found to be true both on foliage in the field and under controlled conditions in the laboratory. This tendency is evident in Fig. 1 and 2.

Changes in temperature, of course, produce corresponding changes in the vapor pressure of each substance, and thereby alter the rate of evaporation or residue loss. The work in progress at Illinois showed definitely that, although changes in temperature affected rates of evaporation or residue loss, in general they produced somewhat corresponding effects on all of the materials studied, as shown for aldrin and DDT in Fig. 4. While an increase in wind or air movement tends to accelerate the rate of residue loss, it affects all materials more or less alike and does not greatly alter their relative positions.

A review of all the conflicting data obtainable led to the obvious conclusion that several factors influence the rate of evaporation and that vapor pressure alone is not an accurate measure of that loss. This is particularly true for the initial period of each test when the spray is being applied and drying on the surface; and it is evident throughout some tests. Evaporation, therefore, must be considered as the summary effect of the various factors which influence residue loss through vaporization: vapor pressure (probably the most important), ratio of mass to surface exposed, air movement, type of formulation used, etc. It follows logically, then, that a substance like DDT, with a vapor pressure of approximately 3.3×10^{-7} at 25° C., exposed as a mass in an open container would lose weight very slowly and might be considered practically nonvolatile. As a thin layer of fine, fluffy crystals exposed to warm, moving air, the rate of loss would be increased manyfold, and it might then be regarded as fairly volatile.

Presumably evaporation has been established as an important, if not a dominant, factor influencing residue persistence for many of our presently used and potentially available insecticides. That brings us back to Fleck's highly significant statement (1948:706–708), "The residual action of an insecticide is determined by its vapor pressure, its sticking power, its solubility, its absorption into the surface to which it is applied, and its resistance to chemical change."

In most instances one should know or determine in advance the relative importance of such factors as solubility, resistance to chemical change (stability), and probability of absorption into plant tissue or coatings. Such factors can then be properly evaluated or eliminated from further consideration. That leaves vapor pressure and sticking power to be considered, and to these I would add the probability of dilution owing to plant growth and formulation variables. While there would, of course, be exceptions to the rule, it is quite probable that the last three factors would apply about equally or proportionately to all pesticide deposits that may come under consideration. That is, regardless of the pesticide used, the factor of plant growth would diminish or dilute all equally. Likewise, in the case of sticking properties and formulation variables, it seems probable that the methods of formulation and application employed would determine tenacity and would apply equally to all materials without regard to their toxicity or volatility. If three of the four big factors—tenacity, dilution by plant growth, and differences at-

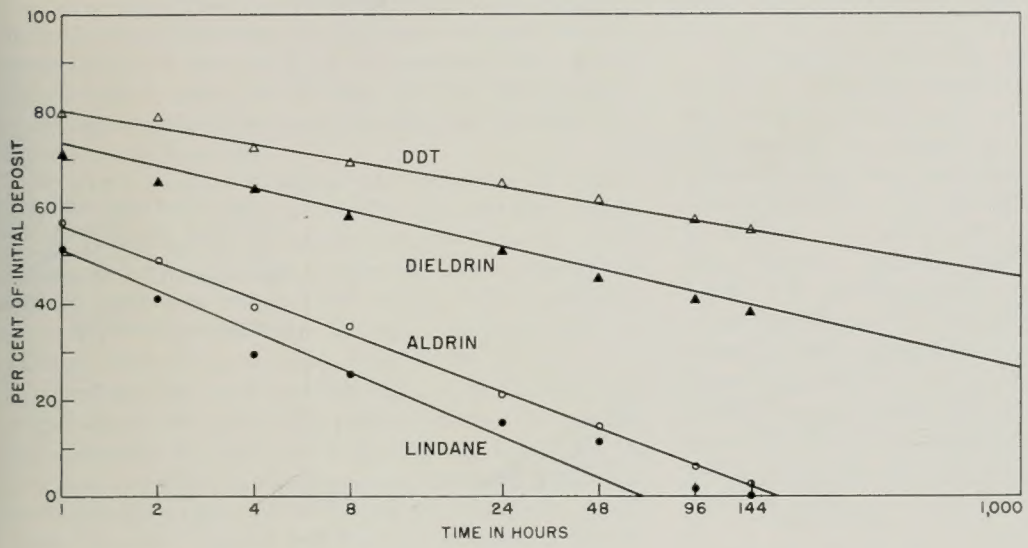

Fig. 3.—Average per cent of initial residue remaining at intervals after 20 by 20 inch filter papers bearing 10 mg of several insecticides were placed in a constant temperature chamber at 80°F.

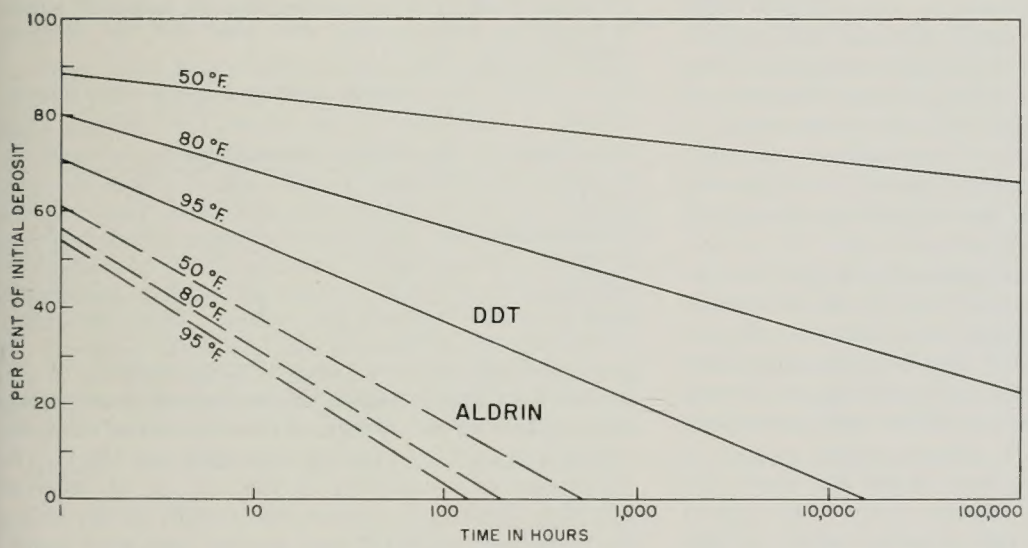

Fig. 4.—Average per cent of initial residue remaining at intervals where 10 mg deposits of aldrin and DDT were exposed on filter papers to varied temperatures.

tributable to formulation—apply about equally to all residues, vapor pressure remains the one important variable which might largely determine relative persistence of the residues produced by various pesticidal chemicals.

PRACTICAL APPLICATION OF GENERAL PRINCIPLES

What are the practical implications or considerations involved? Presumably we are interested in residues primarily for their public health aspects. Therefore, our first concern should be how we may most efficiently utilize chemicals to control pests and at the same time assure the public the greatest possible degree of safety. Where we have a choice of pesticides that will do a given job, we must decide in each instance which of the materials available will be most effective and which can be used with the greatest degree of safety.

Obviously, the inherent toxicity of the chemicals in question to man and other warm-blooded animals must be taken into account, but it may be a minor factor and by no means the dominant consideration. Very often one may find that, from the standpoint of residues, the most toxic substance will be the safest one to use by a considerable margin. In most instances, the more toxic chemicals are used or applied in proportionately smaller amounts than are the less toxic materials, and frequently, but not always, the more toxic compounds are the most volatile and are therefore short-lived.

On the basis of data presented and of many fragments of data obtainable elsewhere, one must conclude that the rate of loss through evaporation for an insecticide is basically a function characteristic of that compound (an index combining vapor pressure, size, and shape of crystal formation, etc.). Through all the work in field and laboratory it was noted that the percentage of residue loss from day to day and from week to week was remarkably consistent for each compound and quite or completely independent of the dosage rate or magnitude of the initial deposit. Thus, it appeared that insofar as loss through evaporation is concerned, residues resulting from different rates of application of a given substance

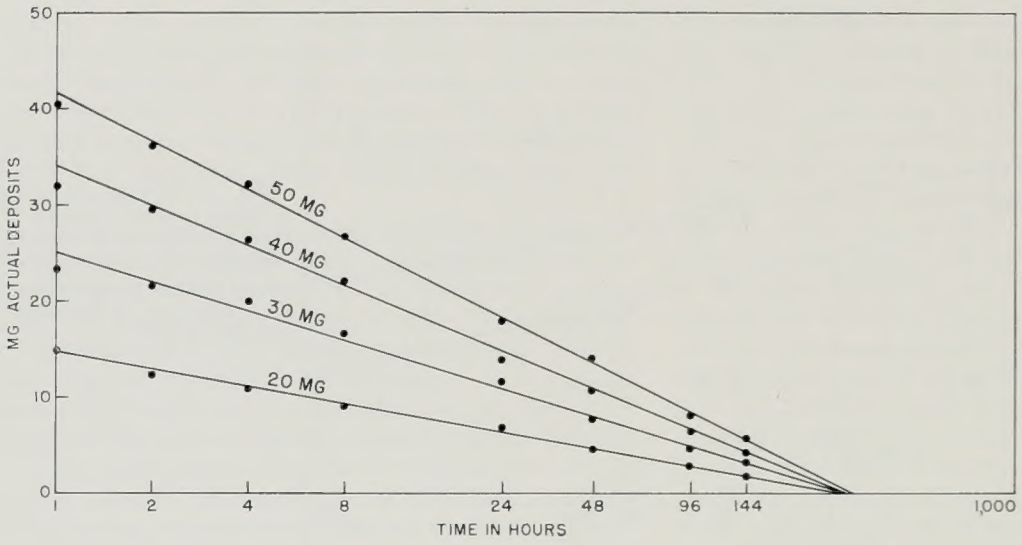

Fig. 5.—Aldrin residues in milligrams at intervals after 20, 30, 40, and 50 mg deposits on 20 by 20 inch filter papers were placed in 80°F. temperature chambers.

will, under the same conditions of exposure, reach the vanishing or zero point at exactly the same time regardless of the magnitude of the original deposits. This sounded logical, but left a feeling of apprehension. In all instances, however, when this theory was tested by exposing various insecticides at varying rates of application, the assumption proved to be valid. All deposits of each compound similarly exposed reached the vanishing point at the same time (Fig. 5).

Now, let us see what the general principles just developed mean in terms of practice. In the first place, with several materials available, what would be the possibility or probability that if used to control a certain pest one or more of the materials would leave a detectable residue at harvest time? Where adequate experimental data are available, the answer to that question is fairly simple. Since it has been shown that under any given set of conditions the residues produced by a given insecticide will arrive at the vanishing point or zero level at a specific time, regardless of the rate of application or the magnitude of the initial deposit, a very good indication of which materials will be most likely to show residues at harvest time can be obtained from Fig. 1, 2, and 3. They indicate the time required for the residue of each material studied to reach the base line or zero point. Obviously, lindane would have the best chance of showing no residue, followed in order by aldrin, chlordane, dieldrin, toxaphene, and DDT, with little likelihood that a DDT residue will ever reach the vanishing point unless aided very materially by other important factors, such as plant growth or erosion. Some idea of the odds that residues of the various materials would be gone by harvest, or by any other given time, might be obtained by comparing the data on days required to reach zero (Table 3).

From these data, which may be subject to considerable error, one may get a fair picture of the relative importance and apparent practical value of several factors that affect the rate of residue loss. From the laboratory data one obtains a forceful impression of the difference in evaporation rates of the semivolatile materials, such as lindane and aldrin, in contrast to the relatively nonvolatile materials, such as toxaphene and DDT. The importance of evaporation in the case of all materials including dieldrin is evident, but a study of the values for toxaphene and DDT discloses the very great significance of erosion and weathering where mature foliage was involved, and the added effect of plant growth in diluting the residue in the case of the growing clover plants.

TABLE 3.—Days of exposure required for residues of various insecticides to decline to zero point under field and laboratory conditions.

Insecticide	Approximate Days Required to Reach Zero		
	Fruit Foliage	Clover Plants	Lab. Papers at 80°F.
Lindane	15	—	3.5
Aldrin	22	15	7.1
Technical aldrin	27	—	9.2
Chlordane	35	21	185.0
Dieldrin	45	25	2,200.0
Toxaphene	85	40	140,000.0
DDT	105	50	210,000.0

APPLICATION OF MATHEMATICAL PRINCIPLES

Assuming that the interval between the date of last treatment and harvest will be such that none of the materials, not even lindane, will have time to vanish completely, the probable magnitude of the residue of any individual compound will be in direct proportion to the dosage rate or the magnitude of the original deposit. As has been shown in the comparison of several dosage rates, since the per cent of original deposit remaining at the end of each interval of time is the same, the residues at any specified interval will be in direct proportion to the magnitude of the original deposit. For example, in Fig. 5, where the original deposits were in the approximate ratios of 2, 3, 4, and 5, the residues remaining in each case on the 1st, 2nd, 4th, and 6th

days were still in those same relative ratios. In addition, the ratios were maintained to the point at which, insofar as the graph is concerned or mathematical calculations can determine, some time on the 12th day (300 hours), according to both theory and practice, all residues disappeared simultaneously.

If one wished to compare two materials, he would have to take into account the slope of the line which can be established by use of the formula $Y = a + bX$ (where X is the logarithm of time; b, the regression coefficient; and a, a constant derived from the equation, $a = \overline{Y} - b\overline{X}$), and the normally recommended or probable rates of application. The higher the evaporation rate and the lower the normally recommended rate of application, the greater the probability that the residue will disappear or reach an insignificantly low level in X days or any other given period. Conversely, the lower the evaporation rate and the higher the dosage or application rate, the greater will be the probability that a very significant residue will be present after any given period.

It is to be hoped that further study of the mathematical principles involved may lead to the development of a formula or formulae which will make it possible to compare two or more insecticides and predict rather precisely the probable relative magnitude of their respective residues X days after treatment, or the relative number of days required for each to reach a residue of Y magnitude. If this becomes a reality, then it will be possible to multiply the values obtained by some suitable index of chronic toxicity supplied by the toxicologist to obtain in advance a fair estimate of the probability that a specified use of a pesticide would result in a significant food contamination hazard. Until such time as suitable formulae are developed, helpful comparisons may be made by utilizing data on dosage rates and 50 per cent or 10 per cent life values.

It is possible also that graphic presentations, such as Fig. 6, will prove helpful in visualization of some of the complex dosage-rate vs. residue-loss relationships. For example, in comparing lindane or aldrin with the reportedly less toxic materials, DDT or toxaphene, one finds that on the 15th day the residues in ppm are, roughly, lindane, 1.0; aldrin, 10; DDT, 152; and toxaphene, 220. On the 20th day they are lindane, 0; aldrin, 2; DDT, 130; and toxaphene, 185. It would appear that in estimating ultimate safety, one would have to balance these or other comparable values for any given time against the relative toxicities of the materials in question. While the ppm lines (Fig. 6) are admittedly calculated from hypothetical considerations, a check on seven points where good data are available indicates all lines are well within a 10 per cent error.

DISCUSSION

The data and discussion presented here in no way establish vaporization as the sole or even the dominant factor in determining the rate of residue losses. We are all too familiar with the importance of weathering, dilution due to plant growth, etc., to discount the importance of these factors. In the field phases of investigations reported here it was impossible to isolate such factors and study them separately. The losses observed in the field investigations were in reality the total accumulative effects of all factors combined. In the final analysis, however, it seems significant that in comparing the residue losses of the different materials tested they tended to persist in the inverse order of their vapor pressures. This could only mean that with the added

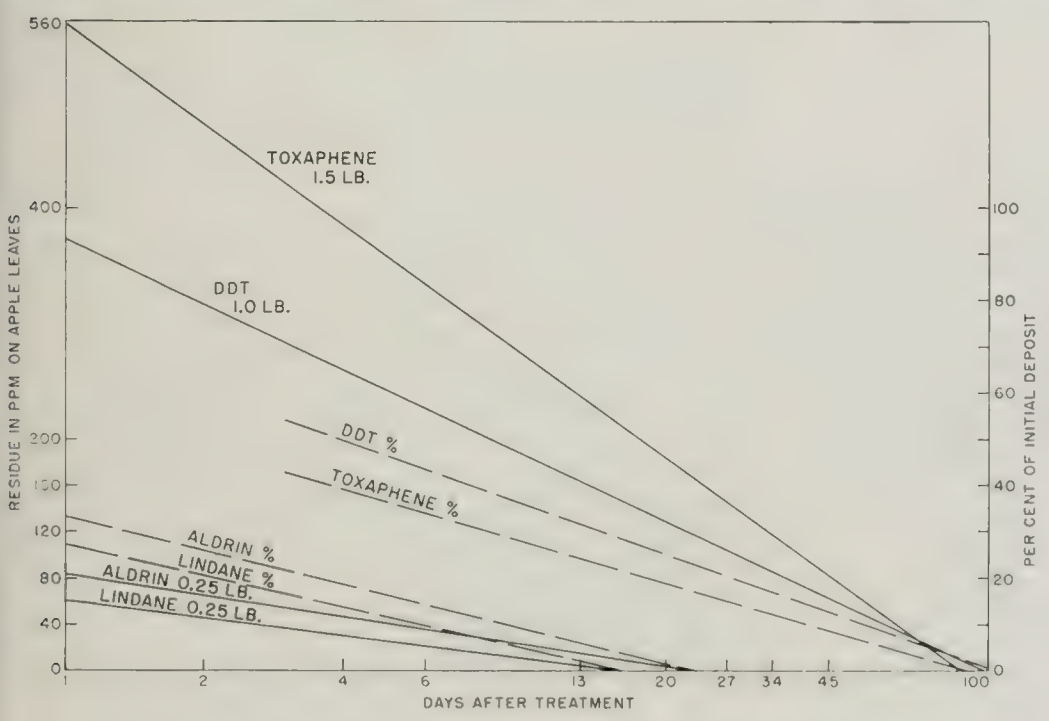

Fig. 6.—Hypothetical residues in parts per million and per cent of initial residue at intervals after treatment, assuming four materials were sprayed on apple foliage at normally recommended rates of application.

advantage of a relatively high vapor pressure, the residue of a given insecticide would tend to disappear more rapidly than the residue of another insecticide lacking high vapor pressure.

Time will not permit a lengthy discussion of other problems, but perhaps the enumeration of a few other practical considerations worthy of thought may be in order.

(1) Where we have been making progressive residue analyses under field conditions, we have found that in some instances after a residue had shown a typical straight-line decline to near zero, we suddenly had a very great rise in the residue level (sometimes 20 to 100 ppm). This was inevitably traceable to drift from other spray operations in the vicinity, in some cases up to 750 feet distant. This raises the question of how much confidence we can place on harvest residues alone unless we are sure beyond doubt that no contamination occurred between our recorded treatment and harvest.

(2) It was observed that where there is any air movement at all, the magnitude of an initial deposit increases row by row from the windward margin of a plot and that there is a very appreciable deposit several rows beyond the plot. One may therefore question the validity of small-plot data.

(3) Since the solvents employed will influence the time of crystallization and the type of crystals produced, to what extent have formulation differences clouded our results and to what extent can we utilize formulation differences to hasten or retard the disappearance of a residue?

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